

Experimental Measurement of Critical Temperature and Critical Density with Differential Scanning Calorimetry. Examples of the Limitations of the Methodology

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Critical properties are synopious with chemical process design. Having said that it is inquilinous that the vapor-liquid critical point is at best weakly defined in comparison with say the triple point. In fact it is best to think of not a point but a region of undefined boundaries where the stability of the system breaks down and the response to a small turbulence is massive in comparison to the size of the disturbance. The practical need is for knowledge of the critical properties of as many substances as possible. Then, corresponding states correlations can be devised and applied to estimate properties away from the critical point. However, the number of substances that are stable at their critical point is limited. Ways of determining the critical properties of compounds that are unstable at their critical temperatures are at a premium.

This paper describes a method developed at the now defunct National Institute for Petroleum and Energy Research in Bartlesville, Oklahoma, USA using a differential scanning calorimeter (dsc) in conjunction with specially designed stainless steel cells to determine the critical temperature and critical density for compounds which are solids or liquids at ambient temperature. The method uses the dsc and the cells of known internal volume to plot out the coexistence curve. Results for stable compounds alkanes, alkenes, aromatics, alcohols, amines, and heteroatom-containing aromatics are discussed. Examples of the use of increased heating rates and/or studies at "low" or "high" filling density to aid in the measurements for unstable compounds are given. Discussion centers on how theory of the actual coexistence curve leads to limitations of the experimental measurement methods.

Coexistence curve results for n-alkanes are compared with Gibbs Ensemble Monte Carlo technique determinations published in the literature by several groups (Zhuravlev and Siepmann, *Fluid Phase Equilibria* **134**, 55; (1997), Cui *et al.*, *Fluid Phase Equilibria* **141**, 45; (1997), and Neubauer *et al.*, *Fluid Phase Equilibria* **155**, 167 (1999). In addition, previously unpublished experimental vapor pressure data on some n-alkanes which are unstable in the critical region allow a direct comparison of simulation data to experimental measurements. The merits of the differing simulations are discussed in terms of which appears to give a picture capable of extrapolations to high molecular weight alkanes producing "realistic" critical properties.